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Photoinitiated Chain Reactions in Low Temperature Solids

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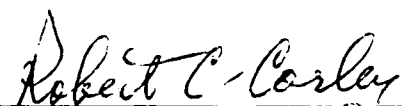
FOREWORD

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This report has been reviewed and is approved for release and distribution in accordance with the distribution statement on the cover and on the DD Form 1473.

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Fundamental aspects of chain reactions in amorphous solid films have been investigated at cryogenic temperatures. Mechanisms of reaction initiation, propagation and termination are described. Most of the experimental studies of this type have been focused on photochlorination reactions of simple hydrocarbons with molecular chlorine in the solid state, photopolymerization reactions of solid formaldehyde, and photodestruction of solid ozone and mixtures of ozone with water and chlorine. Methods have been developed for characterizing the physical properties of vapor-deposited films (van der Waals glasses) at low temperatures. Finally, a simple theory of chain reactions in pure amorphous solids and in binary amorphous solid solutions has recently been developed which accounts for most of the experimental observations made on these systems to date.

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INTRODUCTION

One of the primary goals of the Air Force's High Energy Density Materials Research Program is to identify new materials which might serve the nation's needs for revolutionary (as well as evolutionary) new propellant materials. The search for new metastable species is made difficult because thermodynamic instability is often accompanied by kinetic reactivity. That is, higher energy materials are often the most reactive and therefore the most difficult to store for finite periods of time. An important key to success will be reducing the kinetic reactivity of a solid propellant until it is ignited.

With this in mind, it is likely that any new propellant material will have to be stored as a low temperature solid, or perhaps in a low temperature solid matrix. Our research program was designed to investigate fundamental properties of solid state reactions. While the scope of the project is perfectly general, many of the lessons of our research can guide practical efforts to stabilize and store revolutionary new high energy density propellants whenever specific candidates are identified. In the summary and outlook section of this report, we suggest some possible ways that the reactivity of solid high energy density propellants might be enhanced.

The principal focus of our research has been solid state chain reactions. Chain reactions are undesirable in solid propellants because creation of a relatively small number of reactive intermediates (e.g., free radicals) can lead to conversion of a large number of reactants to products. To illustrate this point, it is worth noting that chain lengths for chlorine-hydrocarbon chain reactions in liquid solutions are typically 10^4. In gases, they can be as high as 10^7. To make matters worse, chain reactions induced in high energy materials might lead directly to detonation of the bulk material.

In order to assess the possible role of solid state chain reactions in future schemes for stabilizing revolutionary new propellants, we decided to investigate some of the fundamental

properties of chain reactions in low-temperature solid films. The compounds and reactions we have studied are not high energy materials or explosives, though it is clear now that some of the techniques we have learned over the past three years can be applied to high energy materials as well as the rather ordinary compounds described in this report.

Our first studies were of reactions between chlorine and simple hydrocarbons in low-temperature solid films. The films were formed by vapor deposition of the gaseous reagents in order to form randomly distributed binary solid solutions of the reactants prior to reaction. Reactions are induced by UV laser photolysis, which creates a small concentration of reactive intermediates within the solid film. Quantum yields for formation of various products are determined by conventional FTIR spectroscopy, UV-VIS absorption spectroscopy, and laser Raman spectroscopy.

Next, we investigated the polymerization of formaldehyde. This system was chosen for detailed study because it is prototypical of chain reactions occurring in pure solids rather than binary solid solutions. We learned techniques of determining reaction quantum yields and average polymer chain lengths.

Ozone was selected for study because it is a participant in several different chain reactions of atmospheric interest. It has also been identified as a possible high energy oxidizing material in advanced propellant formulations. Interestingly, we found that some chain reactions involving ozone in the gas phase are strongly suppressed in the solid state. In fact, we have not yet observed a solid state chain reaction involving ozone.

During the course of our research, we found it necessary to develop new techniques for characterizing the physical properties (density, refractive index, etc.) of vapor-deposited films and thereby gained some limited knowledge about the vapor deposition process itself.

Finally, we have recently developed a simple theory of chain reactions in disordered solids. The theory serves as a framework for interpreting experimental results such as photochemical quantum yields and reaction product branching ratios. In its simplest incarnation, the theory is static. That is, it predicts chain lengths and chain length distributions based on the structure of the solid. For disordered solids, it is assumed that the relevant structural features can be determined on a statistical basis. We have identified important ways in which time-dependent processes such as chain reaction kinetics and heat transport rates can be incorporated into the model. Such an extension will ultimately be important for predicting the stability of amorphous solid propellants. We feel that the development of such an extended model will be a fruitful area of research in which new experiments can directly support and guide the refinement of a practical theory of solid state reaction dynamics.

EXPERIMENTAL TECHNIQUES

Thin amorphous films of chlorine and hydrocarbon or ozone and water are prepared by mixing appropriate quantities of the gases in a glass vacuum manifold, and spraying them onto a CsI, CaF_2 or quartz substrate at 77 K. The reaction cell and general experimental set-up are depicted in Figure 1. The deposition rate of the reagent mixture is typically 0.3 - 0.7 mmoles/hr, and the total amount of sample deposited is typically 0.06 mmoles. The room is kept dark during premixing and deposition of the samples to prevent chain reactions from occurring in the gas phase. The window is held by a copper mount at the end of a stainless steel dewar. Good thermal contact is provided by thin strips of indium foil around the edges of the cold window and between the copper mount and dewar. The entire assembly is mounted within a stainless steel vacuum shroud. The shroud is equipped with one fused silica window through which the samples are irradiated, and two CsI windows for obtaining transmission infrared absorption spectra of the films. The dewar can be rotated while under vacuum so that the window faces the reagent deposition line, the photolysis window, or the IR windows.

Irradiation of the films is accomplished using an excimer laser operating at 308 nm (Questek Model 2200) or a nitrogen laser at 337 nm. After sample deposition, the reaction vessel is closed off and removed from the vacuum manifold. The vessel is placed directly in front of the laser. For the excimer laser each pulse is approximately 15 ns in duration and has a total energy of about 100 mJ which is attenuated with pyrex plates to a fluence $< 4mJ/cm^2$. This is done to minimize the effects of vaporization. The pulse energy is measured using the internal energy meter on the laser, and was verified with an absorbing
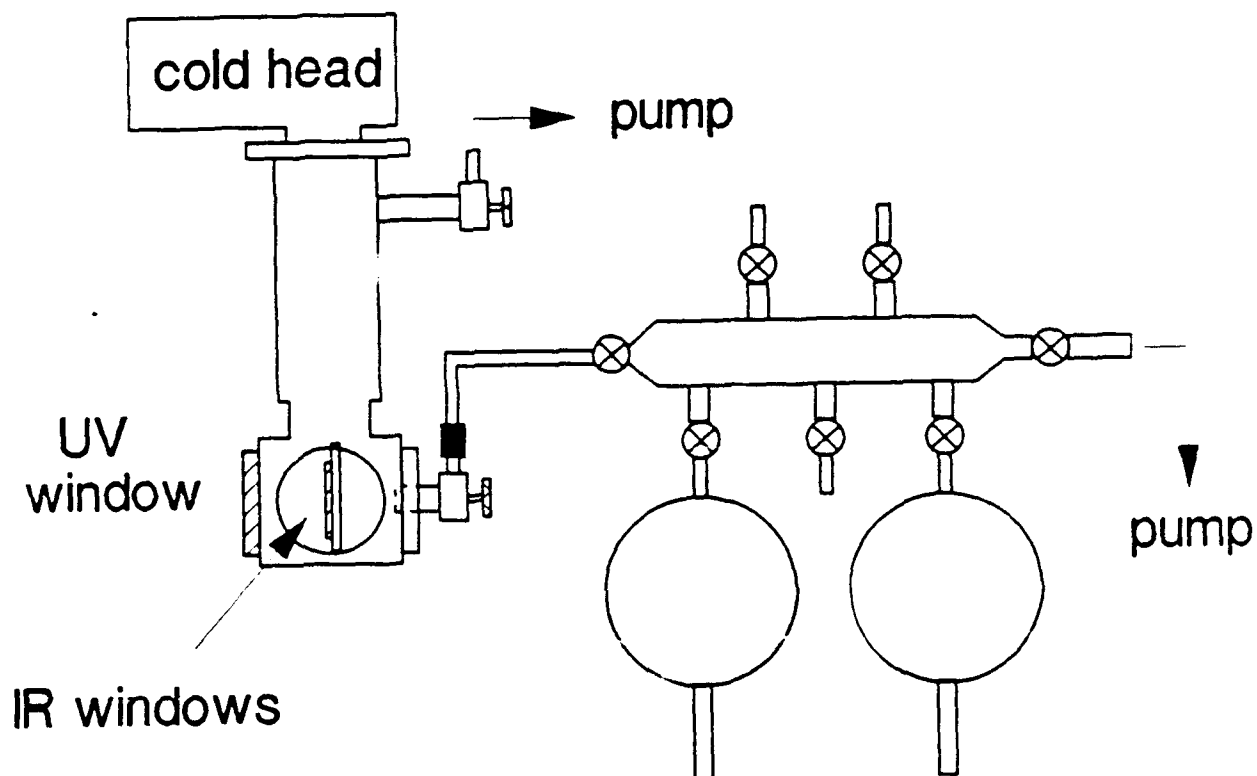
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Figure 1 - Schematic of the reaction vessel for the investigation of reactivity in amorphous solids. The optical substrate (CsI, CaF$_2$ or quartz) is cooled to 10-77 K by either a liquid nitrogen optical dewar (pictured) or a closed cycle helium refrigerator (CTI-cryogenics, model 22C cryodyne cry°ooler). Each sample is prepared by condensing the binary mixture of reagents onto the cold substrate. Following deposition the thin film is photolyzed with either an excimer laser at 308 nm or a nitrogen laser at 337 nm to dissociate either the chlorine or ozone molecules, initiating the reaction. Product yields are then determined by transmission FTIR (Digilab Bio-Rad) and/or UV (Cary 17 or varian DMS-90) absorption spectroscopy.

disc calorimeter (Scientech Model 38-01). The optical density of the samples is typically 0.24 at 308 nm such that 40% of the laser photons are absorbed.

Reaction product yields and branching ratios were determined by Fourier transform infrared absorption spectroscopy (Biorad/Digilab Model FTS-40). Spectra were recorded before and after sample irradiation, and the integrated areas of individual reactant and product bands (in absorbance mode) were used to monitor the extent of reaction. Control experiments in which samples of neat reactants and products were irradiated exhibited slight (1-4%) decreases in the areas of the infrared absorptions. No new bands were observed in these experiments, and the decrease could be attributed either to a slight annealing of the samples or to vaporization of a small fraction of the sample by the laser pulse. This effect was taken into account for samples rich in hydrocarbon when reaction yields were calculated on the basis of diminution of reactant band intensities. In the ozone experiments, the progress of the reaction was monitored primarily by UV absorption spectroscopy (Cary-17 or Varian DMS-90). In these studies the diminution of the Hartley band (200-300 nm) of ozone was followed as a function of the number of laser pulses.

All reagent gases were obtained from Matheson, and have a minimum stated purity of 99.5%. Cyclobutane was purchased from Columbia with a stated purity level of 99%. All other reagent liquids were obtained from Aldrich with a purity of 99%. Chlorine was subjected to repeated freeze/pump/thaw cycles to remove noncondensable impurities. Samples of 1-chloropropane, 2-chloropropane, 1,3-dichloropropane, 1-chlorobutane, 2-chlorobutane, 1,4-dichlorobutane and chlorocyclobutane were obtained from Aldrich (Gold Label, 99%) and were used without further purification. Ozone was prepared by electric discharge of oxygen, followed by distillation.

In order to calculate the reaction yields in the experiment, it is necessary to estimate the number of reagent molecules deposited per unit area at the center of the cold window. Assuming that the sample emerges from the deposition tube with a cosine angular distribution and has unit sticking coefficient, the fraction of the total sample that is deposited in 1 cm^2 at the center of the cold window is calculated to be 11%. This number is obtained by considering the geometry of the deposition orifice and by assuming that the angular distribution of effusing molecules is given by

$$P(\theta,\phi) = \cos^2\theta \sin\theta \, d\theta \, d\phi$$

As a check, the absorbance of a sample containing a known total amount of Cl$_2$ was measured using a Varian Model Cary 17 UV absorption spectrometer. Using the gas phase photoabsorption cross section it was found that 14% of the molecules are deposited per cm^2 at the center of the window. While there is no guarantee that the photoabsorption cross section of gaseous Cl$_2$ at room temperature is the same as that mixed with solid hydrocarbon at 77 K, the good agreement between the two independent methods indicates that our estimate of the two-dimensional sample density is not grossly in error. The 11% figure was used in all of the calculations of product yields.

RESEARCH PROJECTS

Photochlorination of Alkanes

We have investigated photochlorination reactions of several different alkanes during the course of this research project. Most simple alkanes exhibit solid state quantum yields for photochlorination which are less than unity. That is, there is no evidence that chlorination occurs via chain reactions. This is the case for propane, n-butane, isobutane, n-pentane, cyclopentane, n-hexane, cyclohexane, and n-heptane. The small extent of reaction in these cases is attributed to secondary radical recombination reactions. Details are presented in publications 1, 4, and 9 listed on page 17.

Two alkanes we have studied yielded photochlorination reactions significantly in excess of unity. These are cyclopropane and cyclobutane. The key factor which enables chain reactions to propagate in these systems is the a specific mechanism exists for separating radical pairs (e.g., 2 Cl atoms) in the solid state. In the case of cyclopropane, the mechanism is ring-opening. Direct evidence for the stereochemistry of ring-opening was obtained by noting that the solid state chain reaction forms exclusively the anti/anti (AA) conformer of the product, 1,3-dichloropropane. Further details of this study can be found in publications 1 and 4 listed on page 17. In the case of cyclobutane, the radical pair separation mechanism was tentatively identified as being due to symmetric H atom transfer reactions between cyclobutane and cyclobutyl radicals. Details of this study are presented in publication 3.

In both cases where we observed chain reactions, the chain lengths were observed to be much shorter than in liquid solutions or gases. In fact, the maximum chain length observed to date for a solid state reaction is 15 steps. Chain lengths in liquids are typically 10^4 and can be as high as 10^7 steps in gases. The principal impediment to chain propagation in binary solids is believed to be site disorder. That is, each radical intermediate in the chain reaction can react

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with only a limited number of neighboring molecules. In a binary solid, there is a significant possibility that all of these neighboring molecules will be of the wrong type (or possibly the right type but in an unfavorable geometry for reaction with the radical species). This hypothesis is supported by efforts now underway to develop a unified theoretical description of chain propagation in the solid state. It is also supported by annealing experiments. In the latter case, warming allows neighboring molecules to diffuse in the solid lattice. It is observed that the chain lengths of the reaction are significantly extended upon warming to the annealing temperature of the solids.

Polymerization of Formaldehyde

We became interested in studying fundamental aspects of chain reactions in pure (or nearly pure) solids because site disorder should be virtually absent in this case. Polymerization reactions follow this general scheme and it is known from the work of Goldanskii and others that polymerization of formaldehyde can occur in polycrystalline solids at temperatures as low as 4 K. We have prepared amorphous films of formaldehyde containing small amounts of initiator molecules and successfully polymerized these films at temperatures as low as 10 K. Details of our experimental studies on this system are presented in publications 2, 5, 6, and 7.

Initiation of this reaction requires that a strong acid be generated within the solid. This has been accomplished by 1) co-depositing the formaldehyde monomers with small amounts of HCl, 2) photolyzing small amounts of Cl_2 in the solids to form HCl and CHClO, and 3) photolyzing 2-nitrophenol molecules in the solid. This molecule is known to be a weak acid in its ground electronic state, but a strong acid in its excited S_1 state. Any of these three mechanisms is sufficient to induce polymerization of the formaldehyde.

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Again, we observed that polymerization in amorphous films exhibited chain lengths which were much shorter than in polycrystalline solids (work of Goldanskii, et al.). At 77 K, the polymerization chain length in amorphous formaldehyde is 6.5 ± 1. Goldanskii obtained chain lengths up to several thousand monomer units, depending on the temperature of the solid.

In the case of amorphous formaldehyde, the principal limitation to the chain length is believed to be orientational disorder. In each step of the chain polymerization reaction, a new C-O bond is formed. Chain termination (trapping) occurs when the orientations of all the neighboring molecules are such that the reactive site of the growing polymer chain is too far from the oxygen ends of its neighboring monomers.

Photochemistry of Solid Ozone

We became interested in reactions of ozone because this molecule is known to participate in numerous different types of chain reactions, especially of atmospheric interest. Ironically, we have not yet observed a single instance of chain reaction behavior in this molecule. Our one published study is of amorphous solid ozone (pure) and amorphous mixtures of ozone and water. We found that at 308 nm, the quantum yield for photodestruction of ozone was 1.5 ± 0.2. This observation is consistent with an initial photodissociation event in which ozone dissociates to O_2 + $O(^1D)$ with a quantum yield of 0.75. Each excited $O(^1D)$ atom then reacts with another neighboring ozone molecule to form 2 O_2 molecules. The other 25% of photoabsorptive events produces ground state O atoms which are unreactive towards ozone and undergo recombination with O_2 to regenerate the original ozone molecule (no net reaction).

The reaction of ozone/water mixtures is similar in character, except that the $O(^1D)$ + H_2O reaction yields HOOH as the sole product. In the gas phase, this reaction produces 2 OH radicals which serve as chain reaction carriers leading to the destruction of more ozone

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molecules. It is the stabilization of products like HOOH in the solid state which prevents OH formation and suppresses chain reactions in this environment.

We have investigated the quantum yields for photodestruction of ozone and ozone/water mixtures at several different wavelengths. The principal effect of varying wavelength is to change the initial quantum yield of $O(^1D)$ from O_3, and this has a corresponding effect on the overall product yields. All of the evidence obtained to date supports the overall reaction mechanism described above. The variable wavelength experiments are now being prepared for publication.

A few preliminary experiments have been carried out on mixtures of ozone with chlorine at 10 K. No new reactions were observed and the only destruction of ozone was thought to occur by reactions of $O(^1D)$ atoms with O_3 (the same reaction which occurs in films of pure ozone).

Characterization of Amorphous Films

Another area of active investigation is the characterization of refractive index, thickness, and density of thin films formed by vapor deposition. We have developed laser interferometry techniques for doing this. The double-beam methods we had been investigating have proved to be susceptible to large uncertainties due to the fact that the interference fringe patterns obtained at various angles of incidence to the samples are quite similar. A mathematical formalism is being developed which we hope will allow us to determine these physical properties with a single laser beam within acceptable error limits.

We have also investigated fundamental aspects of the vapor deposition process (by which we form amorphous solid films) by examining the propensity for water cluster formation when small amounts of H_2O are deposited with excess nitrogen molecules onto a cryogenic substrate. The results indicate that surface mobility of water molecules is unexpectedly large, and this

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promotes clustering reactions far beyond what would normally be expected from structural (statistical) models of clustering in solids.

We are also attempting to model the vapor deposition process by computer simulation in order to better understand the results of our experimental density measurements and to prepare for experimental measurements of light scattering (Rayleigh and/or Mie scattering). The simplest model involved placement of molecules into a simple cubic lattice at random locations on the surface of the growing film. This model assumes a ballistic deposition process (i.e., one in which the molecule sticks at the first point of contact with the surface and no relaxation of neighboring molecules is permitted). A two-dimensional lattice model predicts a very low density (about 50% of the sites are occupied) whereas the three-dimensional model exhibits a somewhat lower density. The ballistic nature of the models is unrealistic, so we have extended the calculations to include an off-lattice model wherein molecules can contact the surface at arbitrary locations. Techniques which allow relaxation of the molecules in two dimensions have been coded, and we are nearing completion on a three-dimensional model calculation.

Theory of Solid State Chain Reactions

The last area of research undertaken during this project period is development of a percolation theory of solid state chain reactions. A simple static version of the theory has been formulated by considering bond percolation processes on a Bethe lattice. Simple analytical expressions for reaction chain lengths and chain length distributions are obtained which are qualitatively consistent with both computer simulations and the experimental results described above. The theory is flexible enough to treat reaction in pure solids (e.g., polymerization of formaldehyde) and chain reactions in binary solid solutions (e.g., photochlorination of cyclopropane). An outline of this theory are described in an extended abstract prepared for the

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4th annual High Energy Density Contractors Meeting (Air Force) held in Long Beach, CA during February 1990. A more detailed report of the theory and computer simulations of solid state chain reactions will be published shortly [C. A. Wight, "A Percolation Theory of Solid State Chain Reactions", J. Phys. Chem., submitted for publication].

Extensions of the static theory to include time-dependent processes such as chain reaction rates and thermal conductivity are being contemplated. This type of theory would be especially useful when considering reactions of high energy density materials because the evolution of large amounts of heat from chemical reactions can melt local regions of solid propellants, leading to thermal runaway reactions and resulting explosions. It is hoped that a general model such as this will be useful for estimating the stability of a wide variety of energetic materials.

PROJECT SUMMARY AND OUTLOOK

Most of the research carried out under the auspices of this contract has been directed towards understanding fundamental aspects of chain reactions in disordered solids. Some of the things we have learned in the course of this research may have applications in the stabilization of high energy density materials. Some of the important lessons we have learned in this regard are as follows:

- The propagation of chain reactions in amorphous solids is strongly inhibited by two types of disorder. In binary solids, site disorder severely limits the propagation of reactions. In pure solids where site disorder is absent, orientational disorder is effective in limiting the extent of reaction. In revolutionary propellants where the existence of chain reactions can be detrimental to propellant performance, it may be advantageous to store the solids as amorphous rather than crystalline solids because of this advantage.

- Free radical chain reactions are surprisingly difficult to initiate in almost any type of binary solid. Chain reactions of this type have only been observed when a specific mechanism (e.g., ring-opening) exists to efficiently separate radical pairs in the solid state.

- Even in cases where radical production is possible, energy transfer and accommodation in the solid state can alter reaction pathways in ways which inhibit chain reactions. This has been observed in the case of ozone and mixtures of ozone with water or chlorine.

- There are now enough experimental data on solid state chain reactions to begin the formulation of a general model of chain reaction processes in the solid state. The model, though still in its infancy, is nevertheless capable of accounting for most experimental observations to date. We are optimistic that as more systems are studied experimentally we will be able to enhance this model to describe time-dependent as well as static features of the chemical reactivity of disordered solids.

PUBLICATIONS ACKNOWLEDGING AFAL SUPPORT

1. A. J. Sedlacek and C.A. Wight, "Laser-initiated free radical chlorination of propane in amorphous thin films: Temperature dependence from 15-77 K", J. Phys. Chem. 92, 2821 (1988).

2. E. S. Mansueto, C.-Y. Ju, and C. A. Wight, "Laser-initiated polymerization of solid formaldehyde", J. Phys. Chem. 93, 2143 (1989).

3. A. J. Sedlacek and C. A. Wight, "Free radical chain reactions of chlorine with cyclobutane in the solid state: Evidence for radical migration via H atom transfer", J. Chem. Phys. 88, 2847 (1988).

4. A. J. Sedlacek and C. A. Wight, "Photochemical chain reactions in amorphous solids", Laser Chem. 8, 155 (1988).

5. A. J. Sedlacek and C. A. Wight, "Photochemistry of solid ozone", J. Phys. Chem., 93, 509 (1989).

6. E. S. Mansueto and C. A. Wight, "Excited-state proton transfer polymerization of amorphous formaldehyde", J. Am. Chem. Soc. 111, 1900 (1989).

7. C. A. Wight, T. W. Tang, and E. S. Mansueto, "Laser-Induced Reaction and Polymerization of Formaldehyde in Low Temperature Amorphous Solids", in Advances in Laser Science-IV, J.L. Gole, D.S. Heller, W.C. Stwalley, M. Lapp, eds. (American Institute of Physics, New York, 1989).

8. C. A. Wight, T. W. Tang, and E. S. Mansueto, "Low Temperature Photochemistry in Amorphous Films", SPIE Proceedings 1056, 203 (1989).

9. C. A. Wight, P. M. Kligmann, T. R. Botcher, and A. J. Sedlacek, "Photochlorination of simple alkanes in cryogenic solids", J. Phys. Chem. 94, 2487 (1990).

RESEARCH PRESENTATIONS

Invited Lectures

1. "Laser-Induced Reactions of Free Radicals in Low Temperature Solids", University of Colorado, October 1987.

2. "Laser-Induced Reactions of Free Radicals in Low Temperature Solids", University of California at Irvine, October 1987.

3. "Laser-Induced Reactions of Free Radicals in Low Temperature Solids", California Institute of Technology, October 1987.

4. "Free-Radical Chemistry in Low Temperature Solids", University of Colorado at Colorado Springs, March 1988.

5. "Free-Radical Chemistry in Low-Temperature Solids", Brigham Young University, April 1988.

6. "Photochemical Chain Reactions in Amorphous Solids", Furman University, April 1988.

7. "Photochemical Chain Reactions in Amorphous Solids", University of Virginia, April 1988.

8. "Photochemical Chain Reactions in Amorphous Solids", University of Delaware, April 1988.

9. "Photochemical Chain Reactions in Amorphous Solids", Symposium on Dynamical Processes in Condensed Phase, ACS Nat'l Meeting, Los Angeles, September 1988.

10. "State Specific Photochemistry in Cryogenic Solids", Symposium on Structure and Reactivity, University of Texas at Austin, March 1989.

12. "Relationships Between Structure and Reactivity in Amorphous Materials", The Aerospace Corporation, July 1989.

13. "Relationships Between Structure and Reactivity in Amorphous Materials", Astronautics Laboratory (AFSC), July 1989.

14. "Percolation Chemistry: Effects of Disorder on Chain Reactions in Disordered Solids", Symposium on Kinetics of Inhomogeneous Systems, ACS Rocky Mountain Regional Mtg., June 1990.

Contributed Presentations

1. "Photoinitiated chlorination of paraffin hydrocarbons in low- temperature thin films: Cl + C_3H_8", (poster session) ACS national meeting, Denver, CO, April 1987.

2. "Free radical chain reactions in low-temperature solids", (poster session) 1987 Conference on Dynamics of Molecular Collisions, Wheeling, W.Va., July 1987.

3. "Laser Photochemistry in Low Temperature Amorphous Solids", 3rd Annual MFEL Contractor's Meeting, Salt Lake City, May 1988.

4. "Photo-Induced Oligomerization of Amorphous Formaldehyde", (poster session) 3rd Annual MFEL Contractor's Meeting, Salt Lake City, May 1988.

5. "Reaction Dynamics in Molecular Solids: Laser-Initiated Chlorination of Small Hydrocarbons", (poster session) 3rd Annual MFEL Contractor's Meeting, Salt Lake City, May 1988.

6. "Laser-Induced Reaction and Polymerization of Formaldehyde in Low Temperature Amorphous Solids", 4th International Laser Science Conference, Atlanta, October 1988.

7. "Photo-Acids: Solid State Chain Reactions", XVIII Informal Conf. on Photochem., Santa Monica, CA, January 1989.

8. "Low-Temperature Photochemistry in Amorphous Films", SPIE-OE/LASE Conf., Los Angeles, January 1989.

9. "Percolation Chemistry: Chain Reactions in Disordered Solids", (poster session) ACS National Mtg., Boston, April 1990.

10. "Percolation Chemistry: Chain Reactions in Disordered Solids", (poster session) Gordon Conference on Energetic Materials, New Hampton, NH, June 1990.